

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

0 051 810
A1

US 4 311 629



(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 81109130.5

(22) Date of filing: 28.10.81

(51) Int. Cl.³: **C 08 G 77/18, C 08 G 77/06,**
C 09 D 5/14, A 01 N 55/04,
C 08 L 83/08, C 09 D 3/00(30) Priority: 12.11.80 US 206295(43) Date of publication of application: 19.05.82
Bulletin 82/20(84) Designated Contracting States: **DE FR GB IT NL SE**(71) Applicant: **AMERON, INC.**, 4700 Ramona Boulevard,
Monterey Park California 91754 (US)(72) Inventor: **Gysegem, Albert Peter**, 41359 Sylvester Drive,
Lebanon Oregon 97355 (US)(74) Representative: **Patentanwälte Grünecker, Dr. Kinkeldey**
Dr. Stockmair, Dr. Schumann, Jakob, Dr. Bezold Meister,
Hilgers, Dr. Meyer-Plath, Maximilianstrasse 43,
D-8000 München 22 (DE)

(54) Method for making antifouling coating composition.

(57) A solution containing hydrolyzed organotin siloxane polymeric material is formed by hydrolyzing an organotin R-oxy siloxane in a water miscible solvent; R being an alkyl or alkoxyalkyl group with less than six carbon atoms. A water immiscible solvent is added and the water miscible solvent and R-alcohol from hydrolysis are removed by distillation. A marine antifouling coating can be made when the water immiscible solvent evaporates from the solution. A preferred embodiment hydrolyzes tributyltin ethoxy-siloxane in ethyl alcohol with xylene as the water immiscible solvent.

EP 0 051 810 A1

1

5

13081:RDS

10 METHOD FOR MAKING ANTIFOULING COATING COMPOSITIONField of the Invention

15 This invention relates to making a solution containing hydrolyzed organotin siloxane polymeric material suitable for use in marine antifouling coatings.

20 Background of the Invention

 Compositions have been developed for protecting marine surfaces from fouling organisms, including a linear or cross-linked polymer having a siloxane backbone and trisubstituted tin radicals such as tributyl tin bonded to silicon atoms by way of an oxygen atom. The biologically active polymer can be used for forming coatings for steel, concrete, or other surfaces exposed to marine environments for inhibiting the growth of fouling organisms. In some 25 embodiments the polymer is present as an additive in a coating composition. In other embodiments the cross-linked polymer forms a portion of the binder of the coating.

30

35

1 U.S. Patent No. 4,080,190 by Law and Gysegem,
which is hereby incorporated by reference, discloses
such compositions with a variety of organotin radicals
and synthesis techniques. The ratio of tin to silicon
5 atoms in the polymer can be varied for obtaining
different properties in the polymer. When the
proportion of tin is low, a cross-linked polymer can
be formed by hydrolysis and polycondensation of a
siloxane-tin precursor. In an exemplary embodiment
10 the precursor is formed by reaction of tetraethoxysilane
or a short chain ethoxysiloxane with a carboxylic acid
derivative containing a tin radical, such as tributyltin
acetate. A prepolymer can be formed by partially or
completely hydrolyzing the precursor. Water and a
15 hydrolysis catalyst such as hydrogen ion or hydroxyl ion
are added to the solvent. Upon evaporation of the
solvent polycondensation occurs, yielding the desired
polymer.

It is sometimes convenient to hydrolyze the
20 precursor to a prepolymer before completing a coating
composition since prehydrolysis can reduce the curing
time of a coating. Polycondensation of the prepolymer
has heretofore been inhibited by retaining the
prepolymer in ethyl alcohol or similar solvent. Ethyl
25 alcohol is a product of hydrolysis of the precursor
when, for example, an ethoxysilicate is employed in
the synthesis. When such a coating is applied,
evaporation of ethyl alcohol results in polycondensation
in the coating.

30

35

1 Ethyl alcohol and similar water miscible solvents
may not be compatible with other ingredients in the
coating composition. This is particularly true when
the coating composition includes a chlorinated rubber,
5 for example. It is therefore desirable to provide a
solution containing polymeric material which is
compatible with such coating compositions.

10 Brief Summary of the Invention

 Thus, in practice of this invention, a solution
containing hydrolyzed organotin siloxane polymeric
material is formed by combining an organotin R-oxy
siloxane, where R represents a group consisting of
15 alkyl and alkoxyalkyl radicals containing less than
six carbon atoms, a water miscible solvent, water,
a hydrolysis catalyst, and a water immiscible solvent.
After hydrolysis of the organotin R-oxy siloxane,
the water miscible solvent and R-alcohol from the
20 hydrolysis reaction are removed by distillation. The
water immiscible solvent, such as xylene, is preferably
added after hydrolysis. Surprisingly, it is found
that precipitation of such polymeric material does not
25 occur from the water immiscible solvent.

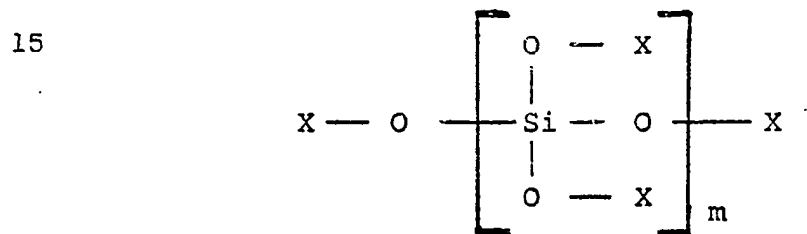
30

35

1 Description

As used herein, the term "precursor" refers to an organotin R-oxy siloxane where R represents a group consisting of alkyl and alkoxyalkyl radicals containing less than six carbon atoms, the term "prepolymer" refers to a precursor that is partly or completely hydrolyzed but not completely condensed; the term "polymer solution" refers to a solution of a water immiscible solvent containing a polymeric material; and the term "polymer" refers to a thoroughly polycondensed prepolymer including linear and/or cross-linked polymers.

Precursors for forming prepolymers for marine antifouling compositions have the formula



20 where m is from about 1 to about 10; where each X is independently selected from the group consisting of R and Y; where each Y in the precursor independently is a trisubstituted tin radical having the formula



30 where R_1 , R_2 , and R_3 are independently selected from the group consisting of alkyl, cycloalkyl, and aryl radicals, where R_1 , R_2 , and R_3 contain in combination up to about 18 carbon atoms, and where the X's are selected

1 so that the ratio of tin atoms to silicon atoms
in the precursor is in the range of from about 1:50
to about 1:1. The Y's in the precursor can be the same
or different. Depending upon the ratio of tin atoms
5 to silicon atoms in the precursor and the nature of
the R_1 , R_2 , and R_3 groups on the tin, the precursor
can be a liquid or a waxy solid at room temperature.

In a mixture of precursor molecules, m represents
the average number of silicon atoms per precursor
10 molecule. Generally there is a random distribution of
molecules comprising more and less than m silicon atoms.
For example, where m equals 5, precursor molecules
containing predominantly 4, 5 or 6 silicon atoms are
present. A few molecules with larger and smaller
15 numbers of silicon atoms can also be present.

In the above formula for the precursors, preferably
m is less than about 10 so the precursor can be
polymerized by hydrolysis and polycondensation.
Preferably m is an average of about five. Such a
20 material comprises a mobile liquid with a high SiO_2
content having ample side groups for substitution of
tin radicals and subsequent hydrolysis and
polycondensation. A suitable material is available
from Union Carbide Chemical Company as "Ethyl Silicate
25 40". This is an ethyl polysilicate or ethoxysiloxane
having an average of about five silicon atoms per
molecule, that is, m equals five, although individual
molecules may comprise as few as one silicon atom.
This material has an SiO_2 content of about 40%.

30

35

1 R comprises alkyl and alkoxyalkyl radicals
containing less than about 6 carbon atoms so that the
alcohol analog of R formed during hydrolysis of the
precursor has sufficient volatility for distillation.
5 Generally, the higher the molecular weight of R, the
lower the volatility of its alcohol analog. Exemplary
of the radicals which R can be are methyl, ethyl,
n-propyl, isopropyl, n-butyl, isobutyl, methyloxymethyl,
methyloxyethyl, and the like. Preferably X is the ethyl
10 radical since transesterification yields ethyl acetate
in a preferred embodiment and hydrolysis yields ethyl
alcohol, each of which is readily removed by
distillation.

15 R_1 , R_2 , and R_3 can be lower alkyl radicals containing
less than about 10 carbon atoms such as methyl, ethyl,
propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl,
hexyl, octyl, nonyl, isooctyl radicals, and the like.
These can also be a substituted lower alkyl radical.
Substituents include chloride, bromide, ether and aryl
20 substituents, and the like.

R_1 , R_2 , and R_3 can be a lower cycloalkyl radical
such as the cyclohexyl radical and substituted lower
cycloalkyl radicals.

25 R_1 , R_2 , and R_3 can be an aryl radical such as the
phenyl radical and substituted phenyl radicals.
Substituents include chloride, bromide, ether, and alkyl
substituents, and the like. Thus R_1 , R_2 , and R_3 can be
chlorophenyl, bromophenyl, nitrophenyl, tolyl, xylyl,
ethylphenyl, and the like. When R_1 , R_2 , and R_3 are all
30 aryl radicals and the precursor has a tin to silicon

1 atom ratio of about 1:5, the prepolymer is a solid
with only slight solubility in common solvents. Thus,
if the prepolymer is to be used for forming a binder
for coating compositions, R_1 , R_2 , and R_3 generally
5 cannot all be aryl radicals.

Preferably, R_1 , R_2 , and R_3 are the same because
trisubstituted tin compounds where the tin is
substituted with the same radical are commercially
available. However, R_1 , R_2 , and R_3 can be different
10 such as where Y is the octyl-dimethyl tin radical.

The total number of carbon atoms comprising a
trisubstituted tin moiety has a large effect on its
biological activity. The effect appears to be one
of size rather than chemical or electronic effect.
15 For example, the octyldimethyl and the tributyl tin
radicals, which have about the same number of carbon
atoms, exhibit about the same toxicity toward mammals
and fouling organisms. In general, small moieties,
such as the trimethyl tin and triethyl tin radicals,
20 show only slight toxicity toward bacteria and marine
fouling organisms, but extremely high toxicity toward
mammals, including man. Tripropyl tin and tributyl tin,
on the other hand, exhibit low toxicity toward man,
but are the most effective trialkyl tin compounds for
25 antifouling use. As the total number of carbons in a
trialkyl tin compound increases above about 12 to 14,
both the human toxicity and antifouling activity
decrease due to the increase of the total number of
carbon atoms.

30 Preferably, when R_1 , R_2 , and R_3 are alkyl radicals,
the total number of carbon atoms in R_1 , R_2 , and R_3 in

1 combination is less than about 14 carbon atoms for high
biological activity. Generally, R_1 , R_2 , and R_3 contain
less than about 18 carbon atoms in combination so that
compositions effective in protecting materials from
5 growth of marine organisms can be prepared.

Preferably, R_1 , R_2 , and R_3 are selected so that
Y is the tributyl, tripropyl, triphenyl or tricyclohexyl
tin radical. These radicals are preferred because they
are broad-spectrum toxicants, especially for many marine
10 organisms, and display minimal toxicity to man. The
tributyl tin radical is particularly preferred.

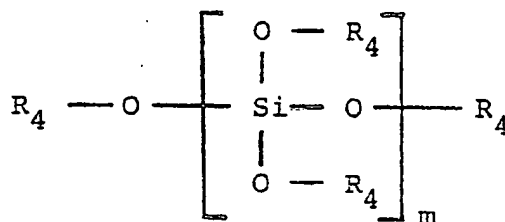
A precursor preferably has a ratio of tin to silicon
atoms greater than about 1:50 because at ratios less than
about 1:50 a coating prepared with the prepolymer shows
15 inadequate biological activity to be of much commercial
value. The maximum ratio of tin to silicon atoms in the
precursor is preferably about 1:1. If the ratio is
higher than about 1:1 steric hindrance by the tin moiety
may inhibit extensive polycondensation and significantly
20 limit the molecular weight of the resultant polymer.

The optimum tin to silicon atom ratio of a prepolymer
used for forming a binder is a balance of competing
considerations. On one hand, the higher the tin to
silicon atom ratio, the more effective and more
25 long-lived is a coating including the prepolymer.
However, at higher ratios of tin to silicon atoms,
curing of the prepolymer by hydrolysis and
polycondensation to form a polysiloxane becomes
progressively more difficult. At tin to silicon atom
30 ratios greater than about 2:5, the prepolymer is not
suitable for preparing binders for coating compositions

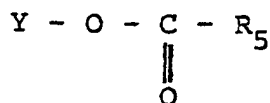
1 because the polymer remains soft and does not cure to
 sufficient hardness to be used as a coating. It is
 believed that a prepolymer having a tin to silicon
 atom ratio greater than about 2:5 is unsatisfactory
 5 for forming binders because the bulky organotin group
 prevents polymerization by either blocking the attack
 of water on the reactive sites of the precursor, or
 by inhibiting condensation of the intermediate silanol
 formed during hydrolysis with another silanol group.

10 A prepolymer for forming a biologically active
 polysiloxane binder preferably has a tin to silicon
 atom ratio of from about 1:12 to about 1:3. In this
 range it has been found that a hard, clear,
 solvent-resistant film exhibiting effective and
 15 long-lived biological activity in preventing fouling
 on marine surfaces can be formed.

The precursor is preferably prepared by reacting
 a silicate having the formula



25 with about n moles per mole of the silicate of a
 carboxylic acid derivative having the formula

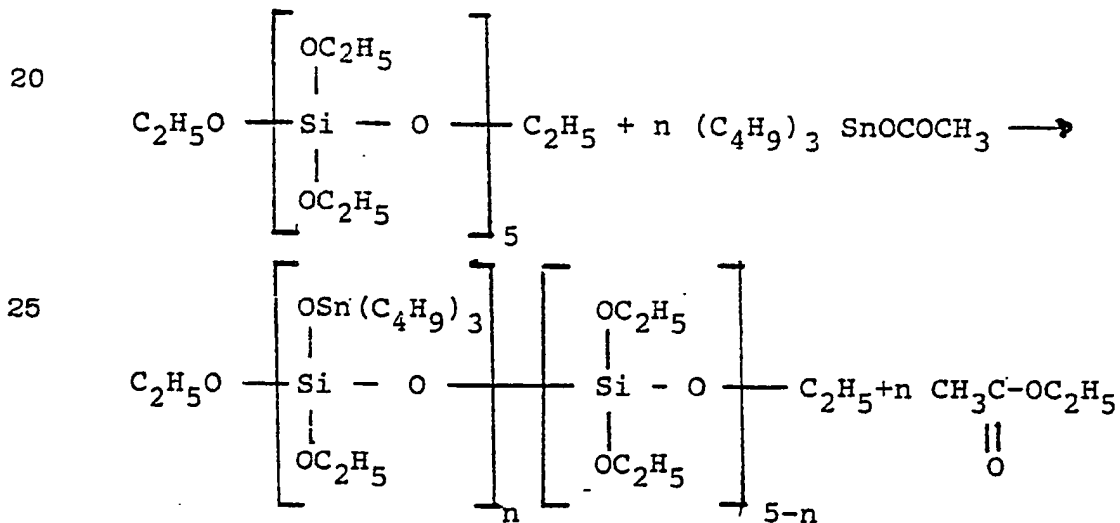


30 where m and Y are as above, and where the ratio of n to m
 is in the range of from about 1:50 to 1:1 to give a
 desired tin to silicon atom ratio as described above.

1 R_4 represents the group consisting of alkyl and
 alkoxyalkyl radicals containing less than about
 six carbon atoms, i.e., R_4 is the organic portion
 of the group from which X is selected. Each R_4
 5 may be the same or different. Preferably, R_4
 is the ethyl radical.

R_5 is selected from the group consisting of
 hydrogen, and alkyl, cycloalkyl, and alkoxyalkyl
 radicals. R_5 is selected for convenience, i.e.,
 10 so that the carboxylic acid ester formed in the
 reaction is sufficiently volatile to be removed
 easily from the product. Preferably a trisubstituted
 tin acetate is employed.

Exemplary of silicates and carboxylic acid
 15 derivatives which can be used are "Ethyl Silicate
 40" and tributyltin acetate. "Ethyl Silicate 40"
 and tributyltin acetate react according to the
 equation



30 The tributyltin substituted silicon atoms are randomly
 located along the chain, and a single silicon atom can
 be substituted by none, one, two or three tributyltin
 groups.

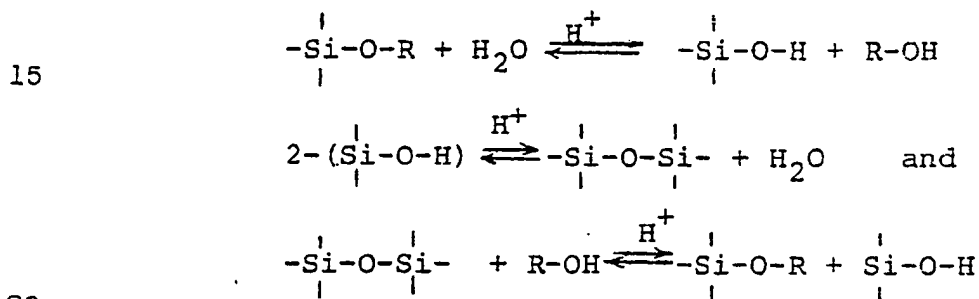
1 The reaction of the silicate and the carboxylic
acid derivative is conducted at an elevated temperature,
and at least at a temperature sufficiently high that
the carboxylic acid derivative melts. The silicate and
5 carboxylic acid derivative are reacted at a temperature
below the temperature at which the precursor prepared
from the silicate and carboxylic acid derivative
decomposes. Decomposition may be evidenced by darkening
of the precursor and a hydrocarbon-like odor. For
10 example, when preparing a precursor from tributyltin
acetate and Ethyl Silicate 40, the temperature should
be maintained from about 160 to about 180°C.

 Another method for preparing the precursor is to
combine a silicate, as described above, with about $n/2$
15 moles of water per mole of the silicate and $n/2$ moles
per mole of the silicate of a bis-trisubstituted tin
oxide having the formula $Y-O-Y$ where Y and n have
the same meaning as above. Generally, a silicate reacts
at a lower temperature with a tin oxide than with the
20 carboxylic acid derivative of the tin oxide. For
example, bis-tributyltin oxide reacts at a fast rate
with Ethyl Silicate 40 in the presence of water at
about 85°C compared to the 160°C required when
tributyltin acetate is used.

25 Another method for preparing the precursors is to
combine a silicate as described above with about n moles
of a trisubstituted tin hydroxide having the formula
 $Y-OH$, where Y and n have the same meaning above, per
mole of the silicate. The silicate and tin hydroxide
30 are combined at a temperature below the temperature at

1 which the precursor formed from the tin hydroxide and
the silicate decomposes.

The fully polymerized polysiloxane is prepared
from the precursor by hydrolysis followed by
5 polycondensation. The hydrolysis of alkylsilicates at
neutral pH is generally too slow to be able to use the
silicate as a binder in coating formulations. However,
in either acidic or basic medium, the rate of hydrolysis
is appreciably increased. In acid conditions, achieved
10 by adding small amounts of an acid to the water used in
the hydrolysis, the equilibrium conditions are reached
in hours. These equilibrium conditions, which are,



all occur simultaneously. Also under acid conditions,
the tendency for linear chain extension and cyclization
is much stronger than for cross-linking. All of these
account for the liquid nature of the hydrolyzed prepolymer
25 when in a closed system where no alcohol can escape. In
the atmosphere, the alcohol can evaporate, thereby driving
the equilibrium toward the condensed silicate form.

30

35

1 Dilute aqueous hydrochloric acid can be used to
catalyze the hydrolysis of the precursor. Other acids
which can be used as catalysts include mineral acids
such as sulfuric acid, orthophosphoric acid, and nitric
5 acid, and organic acids such as trichloroacetic acid,
formic acid and oxalic acid. The amounts to be used
vary for each acid, but the optimum quantity can readily
be determined by a chemist of ordinary skill in the art.
The action of organic acids generally is slower than
10 that of inorganic acids.

Hydrolysis of the precursor can also be catalyzed
by a hydroxyl source which itself is nonreactive with
the precursor, but which reacts with moisture to
produce hydroxyl ions, such as described in U. S.
15 Patent No. 3,653,930, issued to Law et al, and
incorporated herein by reference. This patent
describes catalyzing hydrolysis of silicates with a
hydroxyl source nonreactive with the silicate and
reactive with moisture to produce hydroxyl ions.
20 Exemplary of hydroxyl sources are organic amines
such as mono-, di-, and triethanolamine, diamylamine,
cyclohexylamine, piperidine, and the like, and
inorganic hydroxyl sources such as potassium, sodium,
and lithium hydroxide.

25 A solvent may also be used with the precursor is
hydrolyzed. Thus, the precursor is dissolved in a
solvent such as ethanol before hydrolysis. Exemplary
of the solvents which can be used are those listed in
Table I of U. S. Patent No. 3,653,930. Preferably,
30 the solvent is the same alcohol as the alcohol from
hydrolysis reaction. For example, when the precursor

1 comprises tributyltin ethoxysiloxane, ethyl alcohol
results from hydrolysis and the preferred solvent is
ethyl alcohol. In practice of this invention, such
solvent is distilled from the solution and it is
5 preferable to recover a single distillate for reuse
in the process or for other uses without further
separations.

It has previously been considered appropriate
to supply a coating composition including a precursor
10 or prepolymer in a package with a hydrolysis catalyst.
For example, a precursor can be packaged with a source
of hydroxyl ions so that upon addition of water,
hydrolysis and polycondensation can occur. It has
not been considered appropriate to hydrolyze the
15 precursor with hydroxyl ion catalysis an appreciable
time before application as a coating because of the
possibility of premature gellation and short shelf
life. When the precursor is hydrolyzed with acid
catalysis, the precursor, a water miscible solvent,
20 water, and acid can be packaged together for reducing
the curing time of the applied coating. In some
embodiments, the acid catalyzed coating composition
can be provided in a single container. In the acid
catalyzed product, it had previously been considered
25 necessary to prevent evaporation of the alcohol
product of hydrolysis to prevent premature poly-
condensation and less than complete hydrolysis of
the precursor is preferred.

30 It has been found that gellation of the organotin
siloxane can be inhibited by substantially completely
hydrolyzing the organotin R-oxysiloxane and replacing

1 the alcohol from the hydrolysis reaction with a water
immiscible solvent such as xylene. It appears that
some polymerization occurs in the xylene, forming a
5 solution of polymeric material, since the solution
becomes viscous. The polymeric material in the
solution can be considered for two different ranges
of tin to silicon ratio. As pointed out above, when
the ratio of tin atoms to silicon atoms in a polymer
is less than about 2:5, appreciable cross-linking can
10 occur for forming solid films suitable as binders in
coating compositions. When the ratio of tin atoms
to silicon atoms in a polymer is more than about 2:5,
steric hindrances inhibit cross-linking and an
essentially linear polymer is obtained.

15 When the tin to silicon ratio is more than about
2:5, it appears that linear polymerization of prepolymer
occurs as alcohol is distilled from the solution,
resulting in a solution of polymeric material in water
immiscible solvent where the polymeric material may
20 be similar to the polymer obtained by evaporating the
alcohol and forming a film, for example. This appears
so since the solution is somewhat similar to a solution
made by redissolving in water immiscible solvent a film
made by evaporating alcohol from a prepolymer solution.
25 It is believed, however, that the polymeric material in
a solution made by mixing water immiscible solvent
with the water miscible solvent and then distilling
off the water miscible solvent has greater polymeri-
zation than a redissolved polymer. The elevated
30 temperature used for distillation is believed to
promote added polymerization of the polymeric

1 material. It is desirable to directly transfer from
a water miscible solvent to a water immiscible solvent
since appreciably faster and easier than going through
a solid state.

5 When the tin to silicon ratio is less than about
2:5, the prepolymer can cross-link when alcohol
evaporates from a solution. Surprisingly, however,
when a water immiscible solvent such as xylene is
added and the alcohol distilled from the solution,
10 cross-linking is inhibited and a solution containing
organotin substituted siloxane polymeric material
results. Some polymerization of the prepolymer is
believed to occur since viscosity of a xylene solution
is noticeably higher than viscosity of an original
15 ethyl alcohol solution. The polymeric material in the
xylene solution is not completely cross-linked,
otherwise it would not be retained in solution.
Neither the exact state of the polymeric material
nor the reasons for this effect are known. Such a
20 solution cannot be made by redissolving a solidified
polymer since the cross-linked polymer is not soluble
in xylene or similar water immiscible solvents.

Formation of a substantially completely hydrolyzed
solution of polymeric material in a water immiscible
25 solvent can be quite advantageous. By replacing water
miscible solvent with water immiscible solvent, the
polymeric material can be made compatible with a
variety of coating ingredients with which it is not
compatible before hydrolysis and/or in the presence
30 of ethanol or other water miscible solvents. For
example, hydrolyzed polymeric material in xylene is

1 compatible with chlorinated rubber coating compositions.
Further, by this technique, entrapment of residual
ethanol or other product of the hydrolysis reaction
in the coating film is prevented. Polymers with high
5 tin content are particularly susceptible to this
condition.

Preparation of a solution containing hydrolyzed
polymeric material can be understood by reference to
an exemplary embodiment. Thus, for example, tributyltin
10 ethoxysiloxane is dissolved in a water miscible solvent
such as ethanol. This precursor is hydrolyzed by adding
a hydrolysis catalyst and water. Complete hydrolysis
requires one mole of water per two moles of alkyl and/or
alkoxyalkyl groups on the precursor. When the hydrolysis
15 is acid catalyzed, a dilute aqueous solution of acid
can be slowly added to the solution of siloxane in
ethyl alcohol with good stirring. The addition can be
at ambient or elevated temperature up to the temperature
where decomposition of materials commences. When the
20 reaction is catalyzed by hydroxyl ions, a source for
generating hydroxyl ions such as an amine can be added
to the ethyl alcohol solution of siloxane. Water is
then slowly added to the well stirred mixture at ambient
or elevated temperature. Additional ethanol is a
25 product of the hydrolysis.

A nonreactive or water immiscible solvent such
as xylene is added before, during, or after the
hydrolysis. It can be desirable to add the water
immiscible solvent after hydrolysis in the case of
30 acid catalysis and before hydrolysis in the case of
hydroxyl catalysis.

1 When the hydrolysis is complete and the water
immiscible solvent has been added, temperature is
raised sufficiently to remove ethanol by distillation.
The product is a solution of hydrolyzed polymeric
5 material with a concentration dependent on the amount
of water immiscible solvent added.

Although the example employs a specific soloxane
and specific solvents, it will be apparent that a
variety of materials as outlined above can be employed.
10 Preferably, the water miscible solvent is the same
alcohol as results from the hydrolysis reaction.

The water immiscible solvent is preferably
xylene which is compatible with the ethyl alcohol of
the preferred embodiment, as well as being a good
15 solvent in coating compositions. Ethyl alcohol can
be readily distilled from such a mixture. Other
suitable solvents can be selected from the water
immiscible solvents set forth in Table I of U. S.
Patent No. 3,653,930, incorporated by reference
20 hereinabove. Additional exemplary water immiscible
solvents include halogenated solvents such as
methylene chloride, carbon tetrachloride, trichloro-
ethylene and trichlorotrifluoroethane; various alkanes
such as pentane, hexane, octane or cyclohexane, or
25 low melting waxes, some acetates such as sec-
butylacetate and tert-butylacetate; benzene; naphtha;
toluene; methyl isobutyl ketone; mineral spirits;
gasoline; turpentine, lograine, kerosene, and the
like. The water immiscible solvent preferably has
30 a higher boiling point than the water miscible solvent

1 or R-alcohol product of hydrolysis so that they can
be removed by distillation. Other techniques for
removing the water miscible solvent, such as a molecular
sieve, can also be employed in some embodiments.

5 Such a solution containing polymeric material can
be mixed with a variety of ingredients for forming
compositions for forming marine antifouling coatings.
A broad variety of solvents, thixotropic agents,
fillers, pigments, binders, and the like for marine
10 antifouling coating compositions will be apparent.
Oil based and water based paints, organic polymer
coating compositions such as acrylic, polyethylene,
polypropylene, polystyrene, polyurethane, polyvinyl-
chloride, chlorinated rubber, alkyd resins, and similar
15 coating materials can be included. Diluents, fillers,
and pigments can be included in a coating composition
such as talc, limestone, diatomaceous earth, clay,
iron oxides, zinc oxides, lead oxide, titanium,
dioxide, zinc dust, silica, wollastonite, barites,
20 barium metaborate, chrome yellow, chrome green, copper,
copper oxide, and the like. Organic dyes may also be
used to color the product.

These and other features of the present invention
will be further understood by reference to the following
25 Examples.

EXAMPLE I

A precursor is formed by reacting 533.2 grams of
Ethyl Silicate 40 with 623.7 grams of tributyl tin
30 acetate. Ethyl acetate from the reaction is removed
by distillation yielding 1000 grams of tributyltin

1 ethoxysiloxane or tributyltin ethyl silicate. This
precursor is mixed with 500 grams of ethyl alcohol,
20 grams of 2-ethylaminoethanol and 200 grams of
5 xylene. This solution is heated to about 50°C and
stirred vigorously while 61 grams of water is added
dropwise to the solution over a period of about 15
minutes. The temperature of the solution is then
increased to effect distillation of the ethyl alcohol.
Distillation is complete when 942.5 grams of distillate
10 is collected. The product, comprising a tributyltin
substituted siloxane polymeric material in xylene, is
a viscous liquid.

EXAMPLE II

15 A marine antifouling coating composition is
formulated from a solution containing polymeric
material prepared in accordance with Example I and
contains the following ingredients: 98.0 grams of
tributyltin silicate (from Example I), 77.0 grams of
20 Allopren X-10 (a chlorinated rubber binder), 9.2
grams of coal tar, 36.3 grams of ww rosin, 5.6 grams
of pine oil, 15.8 grams of Shell solvent 1693
(a petroleum distillate), 3.0 grams of Chevron
solvent 265 (naphtha), 39.0 grams of xylene, 1.6
25 grams of methanol, 56.0 grams of zinc oxide, 42.0
grams of red iron oxide, 35.0 grams of talc, and
5.4 grams of Bentone 34 (dimethyldioctadecyl ammonium
bentonite). When this composition is coated on a
substrate and the solvents evaporate, an adherent,
30 tough, somewhat resilient marine antifouling coating
results.

1

EXAMPLE III

5

10

15

20

25

30

35

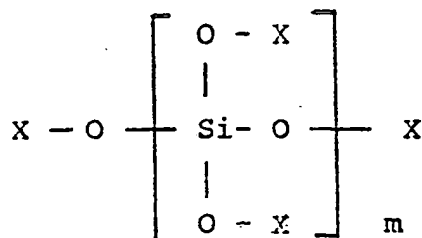
A precursor is formed by reacting 745.2 grams of Ethyl Silicate 40 with 453.3 grams of tributyltin acetate. Ethyl acetate from the reaction is removed by distillation. A solution is formed comprising 200 grams of the resultant tributyltin ethyl silicate in 100 grams of ethanol. The solution is heated to 40°C and stirred vigorously during slow dropwise addition of 17.8 grams of a 2% solution of sulfuric acid in water combined with an equal volume of ethanol. When the addition of this mixture is complete, 50 milliliters of xylene is added to the solution which is then heated to distill the ethyl alcohol. When about 150 milliliters of distillate has been collected, an additional 200 milliliters of xylene is added, distillation is considered complete when a total of 400 milliliters of distillate has been collected. The product is a clear liquid which becomes somewhat cloudy upon cooling. Full cross-linking and precipitation of polymer was not observed. This solution containing polymeric material is useful in a variety of marine antifouling coating compositions.

1 What is claimed is:

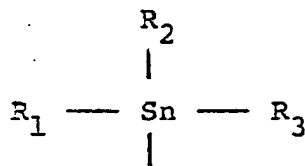
1. A method for preparing a solution containing hydrolyzed organotin siloxane polymeric material
5 comprising: combining an organotin R-oxy siloxane in which the ratio of tin atoms to silicon atoms is in the range of 1:50 to 1:1, where R represents a group consisting of alkyl and alkoxyalkyl radicals containing less than six carbon atoms, a water
10 miscible solvent, water, and a hydrolysis catalyst, characterized by including a water immiscible solvent and after hydrolysis of the organotin R-oxy siloxane, removing by distillation the water miscible solvent and R-alcohol from the hydrolysis reaction.
15
2. A method as recited in Claim 1 wherein sufficient water is combined for substantially completely hydrolyzing the organotin R-oxy siloxane.
- 20 3. A method as recited in one of the preceding claims wherein the water miscible solvent comprises R-alcohol.
4. A method as recited in Claim 3 wherein R is
25 the ethyl radical.
5. A method as recited in one of the preceding claims wherein the water immiscible solvent comprises xylene.
- 30 6. A method as recited in one of the preceding claims wherein the water immiscible solvent is added after hydrolysis and before distillation.
- 35 7. A method as recited in one of the preceding claims wherein the ratio of tin atoms to silicon atoms in the organotin R-oxy siloxane is less than about 2:5.

1. 8. A method for preparing a solution containing hydrolyzed organotin substituted siloxane polymeric material comprising the steps of:

combining a precursor having the formula:



where m is from about 1 to about 10, each X is independently selected from the group consisting of R and Y, R is selected from the group consisting of alkyl and alkoxyalkyl radicals containing less than about six carbon atoms, and each Y is independently a trisubstituted tin radical having the formula:



where R_1 , R_2 , and R_3 are independently selected from the group consisting of alkyl, cycloalkyl, and aryl radicals, and contain in combination up to about eighteen carbon atoms; a water miscible solvent; water; a source of ions selected from the group consisting of hydrogen ion and hydroxyl ion; and a water immiscible solvent having a boiling point higher than the boiling point of the water miscible solvent; and

after hydrolysis of the precursor removing by distillation the water miscible solvent and R-alcohol from the hydrolysis reaction.

1 9. A method as recited in Claim 8 wherein m is
an average of about five.

5 10. A method as recited in Claim 8 wherein the
water miscible solvent comprises ethyl alcohol.

10 11. A method for preparing a solution containing
hydrolyzed organotin siloxane polymeric material
comprising the steps of:

reacting ethoxysiloxane and a trisubstituted tin
compound selected from the group consisting of
tributyltin acetate and bis-tributyltin oxide for
forming a precursor;

15 dissolving the precursor in ethyl alcohol;
adding water and a source of hydrolysis
catalyst selected from the group consisting of
hydrogen ion and hydroxyl ion to the precursor
20 solution for forming a hydrolyzed prepolymer in
solution in ethyl alcohol;

adding a water immiscible solvent to the solution
of prepolymer in ethyl alcohol; and

removing the ethyl alcohol by distillation.

25 12. A method as recited in Claim 11 wherein the
water immiscible solvent is compatible with a
chlorinated rubber binder for a marine antifouling
coating.

30 13. A method as recited in one of the preceding
claims wherein the hydrolysis catalyst is hydroxyl
ion or hydrogen ion.

35 14. A solution comprising a water immiscible solvent
containing a polymeric material consisting essentially
of hydrolyzed organotin substituted siloxane, where

- 1 the ratio of tin atoms to silicon atoms in the polymeric material is in the range of from about 1:50 to 2:5.
- 5 15. A solution as recited in Claim 14 wherein the water immiscible solvent comprises xylene.

10

15

20

25

30

35



European Patent
Office

EUROPEAN SEARCH REPORT

0051810

Application number

EP 81 10 9130.5

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,X	<p><u>US - A - 4 080 190</u> (G.H. LAW et al.)</p> <p>* column 4, line 18 to column 8, line 47; column 10, line 44 to column 13, line 4; column 13, examples 1 to 3; column 14, example 8; column 16, table 3, example 19 *</p> <p>---</p>	<p>1-5,</p> <p>7-15</p>	<p>C 08 G 77/18</p> <p>C 08 G 77/06</p> <p>C 09 D 5/14</p> <p>A 01 N 55/04</p> <p>C 08 L 83/08</p> <p>C 09 D 3/00</p>
A	<p><u>US - A - 3 392 036</u> (G.D. McLEOD)</p> <p>* column 3, lines 4 to 59 *</p> <p>---</p>	<p>1,3,5</p>	<p>TECHNICAL FIELDS SEARCHED (Int. Cl.3)</p>
D,A	<p><u>US - A - 3 653 930</u> (G.H. LAW et al.)</p> <p>* column 5, table 1 *</p> <p>---</p>	<p>3,5</p>	<p>A 01 N 55/04</p> <p>C 07 F 7/04</p> <p>C 08 G 77/00</p> <p>C 08 L 83/08</p> <p>C 09 D 3/00</p> <p>C 09 D 5/00</p>
A	<p>FARBE UND LACK, Vol. 83, No. 12, 1977</p> <p>J. LORENZ "Bewuchsschutz an Schiffen - eine Standortbestimmung"</p> <p>pages 1072 to 1079</p> <p>* page 1078, paragraphs 9-1,9-2 *</p> <p>-----</p>		<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant</p> <p>A: technological background</p> <p>C: non-written disclosure</p> <p>P: intermediate document</p> <p>T: theory or principle underlying the invention</p> <p>E: conflicting application</p> <p>D: document cited in the application</p> <p>L: citation for other reasons</p>
<p>X The present search report has been drawn up for all claims</p>			<p>&: member of the same patent family, corresponding document</p>
Place of search		Date of completion of the search	Examiner
Berlin		01-02-1982	IDEZ

THIS PAGE BLANK (USPTO)